Food Packaging and Shelf Life 16 (2018) 211–219

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

journal homepage: www.elsevier.com/locate/fpsl

Development of antimicrobial LDPE/Cu nanocomposite food packaging film for extended shelf life of peda

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ARTICLE INFO

Keywords:
Copper nanoparticles
Microwave synthesis
Antimicrobial food packaging film
Improved shelf life

ABSTRACT

Low density polyethylene /copper nanocomposites with strong antimicrobial activity and barrier properties were successfully prepared for active food packaging which showed of extended shelf life of Peda (Indian sweet dairy product). Copper nanoparticles (Cu-NPs) were incorporated from 0.5 wt.% to 3.0 wt.% into a low-density polyethylene (LDPE) matrix by using lab scale doctor blade film applicator to prepare 120 μm thin food packaging films. The effect of different weight percent loadings of Cu NPs on to morphology, mechanical properties of LDPE/Cu nanocomposite films was examined. It was found that Cu-NPS uniformly dispersed into a LDPE matrix and provided improved mechanical properties. There was increment in mechanical properties with decrement in water vapour permeability (WVP) with increase in Cu-NPs amount. LDPE/Cu nanocomposites film also shows superior antimicrobial effect averse to gram +ve and gram -ve food deteriorating microorganisms.

1. Introduction

Over period, consumers are demanding for process and packed food product with extended shelf life. Packaging of food is the final step in food processing industry. With use of food preservation techniques, finished product can be stored for period however the chance of contamination persists. The use of antimicrobial food packaging films can have a significant impact to minimise recontamination and increase in shelf life (Duncan, 2011). The antimicrobial activity of such films can be achieved by incorporating antimicrobial agents in polymer matrix (Azeredo & Henriette, 2009). Inorganic antimicrobial agents like metal and metal oxides are advantageous over organic agents such as organic acids, bacteriocins, enzymes and spices extract etc since they cannot withstand the harsh processing conditions of polymer films (Othman, 2014).

Petrochemical based plastics have been accepted by the food industry since of their obtainability in extents at low price and reason of favourable functional characteristics. These materials are not only flexible and compatible with food stuffs, but are likewise safe, transparent, inexpensive and versatile (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). Compare to other packaging materials, polymeric films are used in food packaging due to their low cost and valuable properties (Akelah, 2013). To maintain freshness and sensory quality of food, it is important that moisture may not permeate in plastic packaging materials during storage. The presence of moisture in food package provides favourable conditions for microorganisms to grow on food surface. Considering all facts, it appears that the suitable material for packaging applications should have sound mechanical properties, high permeability and antibacterial properties. These requirements could be fulfil by embedding appropriate inorganic nanoparticles in a polymeric matrix. (Quintavalla and Vicini, 2002). Application of nanotechnology in packaging film offers a new term nanocomposite (Camargo, Satyanarayana, & Wypych, 2009). Arora & Padua (2010), and Siracusa (2012) reported that nano fillers reinforced polymer films show enhanced barrier properties of nanocomposite food packaging films. The mechanical properties of film can be upgraded with the increasing concentration of nanoparticles in nanocomposites (Grigoriadou et al., 2013; Mishra & Shimpi, 2006; Shimpi, Mali, et al., 2014, Shimpi, Sonawane, et al., 2014, Mishra, Sonawane, Singh, Bendale, & Patil, 2004; Shimpi, Verma, & Mishra, 2010; Sonawane, Mishra, & Shimpi, 2009)

Included in various antimicrobial agents, copper has been known for a long time. Studies on antimicrobial mechanism of Cu-NPs are reported in literature (Caroling, Vinodhini, Ranjitham, & Shanthi, 2015; Chatterjee et al., 2012; Grass, Rensing, & Solioz, 2011; Zain, Stapley, & Shama, 2014) Mechanism of inhibition of growth of microorganisms by Cu-NPs was basically depending on particle size and concentration of nanoparticles. By passaging bacterial cell membrane and then destructing their vital enzymes, Cu-NPs show their efficacy against gram +ve and gram −ve bacteria, high stability and antifungal activity (Vincent, Hartemann, & Engels-Deutsch, 2016). Due to rapid oxidation of Cu° on favourable condition the synthesis of Cu-NPs is very

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https://doi.org/10.1016/j.fpsl.2018.04.001
Received 28 September 2017; Received in revised form 30 January 2018; Accepted 3 April 2018

challenging. Cu-NPs have been produced by different methods viz., micro-emulsion/reverse micelles (Yallappa et al., 2013), laser irradiation (Longano et al., 2012), thermal decomposition (Betancourt-Galindo et al., 2014), chemical reduction (Liu, ZHOU, Yamamoto, Ichino, & Okido, 2012), etc. and many more methods are available in literature. Microwave heating technique is useful for the synthesis of organic compounds, polymers, inorganic materials, and nanomaterials which were introduced in 21st century. By tuning microwave parameters and choice of solvent, nanomaterials can be synthesized using novel green approach of microwave assisted method, which has several advantages over the other like eco-friendly, very short reaction times, mild temperature conditions, one-step synthetic route and low cost are the prime ones (Gawande, Shelke, Zboril, & Varma, 2014).

The focus of study is to develop active food packaging film which fulfils demand for good food packaging film. In the present work, LDPE/Cu nanocomposites were prepared for different concentrations of Cu-NPs. With the help of Cu-NPs dual propose could be achieved to act as effective antimicrobial agent and with increased mechanical as well as barrier properties. The performance of the film was examined on Peda which is having limited shelf life for 24 h only.

2. Materials and methods

2.1. Materials

$CuSO_4$ (Coper sulphate dehaydrated) (Loba Chemical, India), $C_6H_8O_6$ (Ascorbic acid) (Merk, India), Gelatin (Himedia, India), Low density polyethylene (LDPE) was purchased from (reliance industries), Xylene GR (Merk, India).

2.2. Synthesis of Cu-NPs

Highly pure ~50 nm size Cu-NPs were synthesized by microwave method. For the synthesis process 10 mL of 0.1 M $CuSO_4$, 50 mL 1% gelatin solution and 5 mL 0.1 M ascorbic acid were mixed. Colour change is seen at first blue to green on room temperature during mechanical stirring. The contents were then heated to boil in a domestic microwave oven at full power for about 30 s on- off mode of two to three cycles. Green colour of solution changed to yellow, orange and finally wine red coloured Cu-NPs. After centrifugation at 10,000 rpm for 10 min the Cu-NPs were collected in wet form and then vacuum dried at 50 °C for 24 h.

2.3. Preparation of LDPE/Cu nanocomposite film

LDPE/Cu nanocomposites containing 0.5, 1, 1.5, 2, 2.5 and 3 wt. % were prepared by using solvent evaporation and thin film of uniform thickness were prepared by doctor blade film applicator. To prepare films, in 45 m l of xylene, 5 g of LDPE polymer was dissolved at a constant temperature 110 °C using oil bath; Prior, Cu-NPs were dispersed in LDPE/ xylene solution by temperature controlled ultrasonic bath sonicator to achieve proper dispersion. Later, composite films were fabricated on glass plates using doctor blade film applicator (120 microns) at 100 °C. LDPE is high crystalline polymer, which get precipitated if temperature of xylene becomes lower than 150 (± 5) °C. To fabricate a film, glass plate temperature was maintained at 150 °C (Lock, Walton, & Fernsler, 2008). The prepared films were peeled off from glass plates. The Gas Chromatograms (Figs. S1–S5) and FTIR (Fig. S6) were recorded to confirm the residual concentration of xylene in film (Seo & Shin, 2010; Garcia-Turiel & Jérôme, 2007). The results do not show the presence of xylene in the film.

2.4. Analysis of Cu-NPs and LDPE/Cu nanocomposite film

2.4.1. Ultraviolet–visible spectroscopy (UV–vis)

The UV–vis spectra of Cu-NPs was performed on Cary 60 UV–vis spectrophotometer (agilent technologies, India) in the range of 200 nm to 800 nm. To observe optical properties of Cu-NPs.

2.4.2. X-ray diffraction (XRD)

For the determination of crystalline structure of Cu-NPs and LDPE/Cu nanocomposite film, the XRD monochromatic Cu Ka radiation (l 1/4 1.5406 A) at 40 kV° and 40 mA (Model D8 Advance Bruker Limited Germany) was used. The optimization of diffraction patterns was done in an angular range of 5–80 (2θ) with scanning speed of $1^\circ S^{-1}$.

2.4.3. Field-emission scanning electron microscopy (FE-SEM) & energy dispersive spectroscopy(EDS)

The FE-SEM images of the Cu-NPs and nanocomposites films were recorded on FE-SEM S-4800 Type II Hitachi High Technology Corporation Limited, JAPAN. It was operated at 15.0 KeV. The elemental compositions of the samples were determined by EDS.

2.4.4. Particle size analysis

Cu-NPs were dispersed in distilled water to find the particle size using particle size analyzer (Malvern, ZS- 200, Worcestershire UK).

2.4.5. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of gelatin capped Cu-NPs were recorded on 8400 Shimadzu, Japan FTIR, in the frequency range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.4.6. Thermal properties

Shimadzu TGA 50, Japan Thermogravimetric analyzer and Shimadzu DSC 60, Japan were used to study thermal properties of LDPE/Cu nanocomposite films by following the details given elsewhere (Shimpi, Shirole, & Mishra, 2015, Shimpi et al., 2014a, b)

2.4.7. Mechanical properties

Universal testing machine (UTM 2302) supplied by, Hi-Tech machines, Mumbai (India) was used for determination mechanical properties of LDPE/Cu nanocomposite films for testing 2 cm × 5 cm samples strips were cut and tested were carried out 5 times for each sample. Also given in (Shimpi et al., 2015).

2.4.8. Cu^+ ion release study

SL176 double beam atomic absorption spectrometry supplied by Elico science and laboratories. (India) was used to study the quantity of Cu^+ ions released from the LDPE/Cu nanocomposites, three rectangular strips of 2 cm × 2 cm and thickness 120 μ samples were taken and immersed in 15 mL of distilled water for 24 h. This experiment was carried out for 30 days (Shameli et al., 2010).

2.4.9. Water vapour permeability (WVP)

Desiccant method or dry cup setup was in accordance with standard ASTM 96 used. Stainless steel permeability cups with an outside diameter of 62 mm and a height of 38 mm (including clamps) and an inner cup diameter of 35 mm were used. Permeability cup was half-filled with 3 g of anhydrous calcium chloride. LDPE/Cu nanocomposite film was placed over the cup and a 2-mm thick Teflon gasket was placed over the film. The top metal ring was then placed on top of the teflon gasket and secured by three screw retained clamps to ensure a tight seal. The permeability cups were placed in the desiccator filled with water. The relative humidity was 95% during these experiments. The weight gain of cup was measured to the nearest 0.0001 mg by using a precision analytical balance after 24 and 48 h. Three samples for each treatment were tested. The WVP of film was calculated by Eq. (1) reported by Rhim, Mohanty, Singh, and Ng (2006) and Kadam et al. (2017) as given below.

$$WVP = (WVTR \times L)/\Delta P \quad (1)$$

where,